Chem 431A-Lecture 5 10/1/07
admin:
(1) sign attendance sheet.
(2) remind Quiz#2 Wed,
on chapt 1(thermo and genetics, chapt2 acid
base)

Last time:

We reviewed acids and bases.
We started bioenergetic intro
<u>Lecture:</u>
2nd law of thermodynamics:

$\Delta S_{universe} \geq 0$

3 aspects of entropy:
a) energy
b) matter
c) information

Please read and be able to explain and give
examples for the above (see page 24, the
box 1-3)

Here it is convenient to introduce the Gibb's
Free energy, G:

For an isothermal (constant T) system,
$\Delta G = \Delta H - T\Delta S$.

ΔG is useful "chemical work" that a system
can do as a result of the process.

ΔH would represent the "heat content"
$T\Delta S$ represents the "mandatory change in
entropy" as a system changes during a
process.

It can be shown that for a reaction to be
spontaneous, $\Delta G < 0$ (negative). If it is
negative, the system is not only spont., it
also can do work (like make a muscle move
or a cell grow, or protein be synthesized).

This work is measured in energy units (J or cal) and the maximum possible work is equal to ΔG.

In summary, we can write for $\Delta G = \Delta H - T\Delta S$:

ΔH	ΔS	Low T	High T
+	+	$\Delta G > 0$, not fav.	$\Delta G < 0$, favored
+	-	$\Delta G > 0$, not fav.	$\Delta G > 0$, not fav.
-	+	$\Delta G < 0$, favored	$\Delta G < 0$, favored
-	-	$\Delta G < 0$, favored	$\Delta G > 0$, not fav

How do we calculate ΔG? we can calculate in many different ways.
(a) $\Delta G = \Delta H - T\Delta S$
(b) $\Delta G = \Delta G° + RT\ln Q$
(c) $\Delta G° = -RT\ln K_{eq}$

First, for a chemical A, in solution, the G is given by : $G_A = G_A° + RT\ln[A]$
If it goes from A to B as in the rxn:
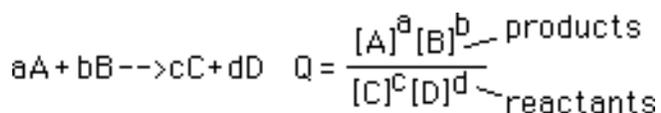   A--> B, then $G_B = G_B° + RT\ln[B]$

And ΔG for the above rxn as written is:
$\Delta G = G_B - G_A = G_B° - G_A° + RT\ln([B]/[A])$
$\Delta G = \Delta G° + RT\ln Q$
Where Q = reaction quotient = [products]/[reactants]

$$aA + bB \longrightarrow cC + dD \quad Q = \frac{[A]^a[B]^b}{[C]^c[D]^d} \begin{matrix} \sim products \\ \sim reactants \end{matrix}$$

If $aA + bB \ddagger cC + dD$ => we can write: $\Delta G = \Delta G° + RT\ln Q$
Where Q = reaction quotient = [prods]/[rxts]
; $Q = [C]^c[D]^d/[A]^a[B]^b$

If we are dealing with a transport process, where in a substance A goes from a compartment (1) thru a semipermeable membrane to compartment (2), we can write for the process $[A]_1 \rightarrow [A]_2$:

$\Delta G = RT\ln([A]_2/[A]_1)$
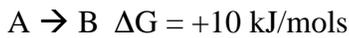
Chemical reactions are often well described by:
$\Delta G = \Delta G^\circ + RT\ln Q$ wherein $\Delta G = 0$ when system is at equilibrium.
($\Delta G = \Delta G^\circ + 2.303 RT \log Q$)

Here, $Q = K_{eq}$ by def and we have $0 = \Delta G^\circ + RT \ln K_{eq}$ and $\Delta G^\circ = -RT\ln K_{eq}$
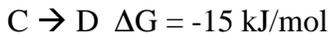
Or, also: $K_{eq} = \exp(-\Delta G^\circ/RT)$

<u>Nonspontaneous reactions can be made spontaneous:</u>

In biochemistry, we often have reactions which appear nonspontaneous.

A → B $\Delta G = +10$ kJ/mols

But it can be spontaneous if <u>coupled</u> to a very exergonic reaction:

C → D $\Delta G = -15$ kJ/mol

So we have:

A+C → B+ D $\Delta G = -5$ kJ/mol

(b) Chemical example

Reaction 2:
ATP → ADP + P_i

Reaction 3:
Glucose + ATP →
glucose 6-phosphate + ADP

Free energy, G

Reaction 1:
Glucose + P_i →
glucose 6-phosphate

ΔG_2

ΔG_3

ΔG_1

$\Delta G_3 = \Delta G_1 + \Delta G_2$

Reaction coordinate

This is a convenient way to determine the ΔG° (by measuring K_{eq}). Recall that ΔG° is the standard free energy change for a reaction. It represents the value of ΔG° when the activities of products and reactants is unity. When all [reactants] & [products] =1 M, then, Q=1 and $\Delta G = \Delta G^\circ$.

In biochemistry, we use $\Delta G^{\circ'}$ the prime (') signifies that the $[H^+]$ is not 1 M but instead that pH = 7. (biochemical reactions are very sensitive to pH and can't function at pH's too far from physiological pH.).
ALL organisms: The free energy released in redox reactions is conserved in the energy carrier molecule adenosine triphosphate (ATP).
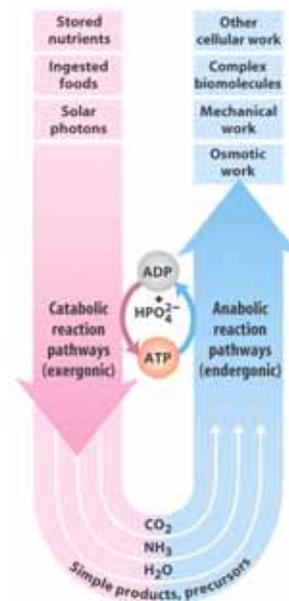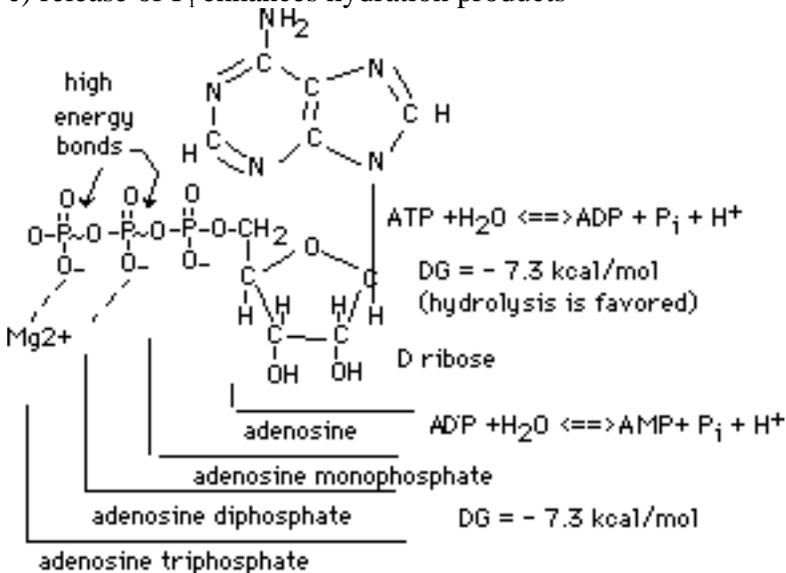
NH_2

HC

CH

O^- O^- O^-
$^-O-P-O-P-O-P-O-CH_2$

H   H

H   H

OH   OH

(P)—(P)—(P)—Ribose — Adenine
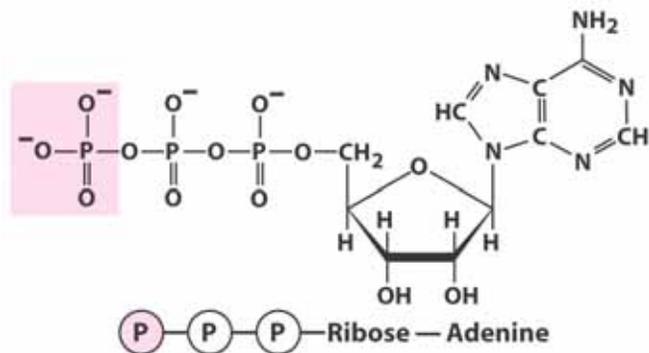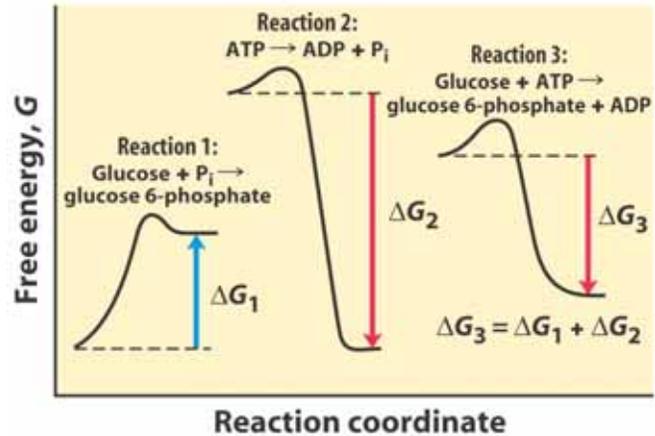
ATP can be hydrolyzed to yield a large amount of energy:

$ATP^{3-} + H_2O \rightarrow ADP^{2-} + HPO_4{}^{2-} + H^+$

$\Delta G^{\circ\prime} = -7.3$ kcal/mol

Source of large $|\Delta G|$ for hydrolysis of ATP to $ADP + P_i$:

a) relieves high charge concentration
b) larger resonance (higher entropy) of P_i
c) release of P_i enhances hydration products

ATP $+H_2O \Longleftrightarrow ADP + P_i + H^+$

DG $= -7.3$ kcal/mol
(hydrolysis is favored)

ADP $+H_2O \Longleftrightarrow AMP + P_i + H^+$

DG $= -7.3$ kcal/mol

other examples of high energy bonds:

e.g. compound	$\Delta G^{\circ\prime}$ (kcal/mol)
phosphoenol pyr	-14.8 (highest P transf pot)
1,3 diphosphoglycerate	-11.8
creatine phosphate	-9.8
ATP (intermediate)	-7.3
glucose-1-phosphate	-5.0
glycerol phosphate (lowest PTP)	-2.2

these are examples of "high energy" compounds or intermediates

Role of enzymes is
a) to speed up reactions (both ways!)
b) to allow coupling of reactions.
c) to promote metabolic pathways
d) to allow regulation of pathways (eg feedback inhibition)

know diff between catabolism and anabolism

section: 1.4 genetic foundations

DNA is the basic genetic material

Linear sequences of DNA encode proteins with information on its amino acid sequences. These in turn are responsible for the unique 3-d native structures of the proteins.

The DNA is passed on during replication of the cell, almost without error. The unmutated are the "wild type" cells,

Errors are more often disadvantageous. Sometimes chance mutations are advantageous and allow for evolution to occur through *selectivity*.

DNA serves as a "historical" document of biological history.

First chapter of evolution: chemical evolution
Oparin's "primordial soup" hypothesis
Stanley Miller's lab simulation of primordial soup: from NH_3, CH_4, H_2O and H_2 => amino acids, hydroxy acids, aldehydes, HCN.

Later: even RNA-like molecs and polypeptides (RNA molecs can act as catalysts)

"RNA World" Hypothesis: RNA was first gene and catalyst
(thru self-replicating RNA)

Evolutionary relationships:
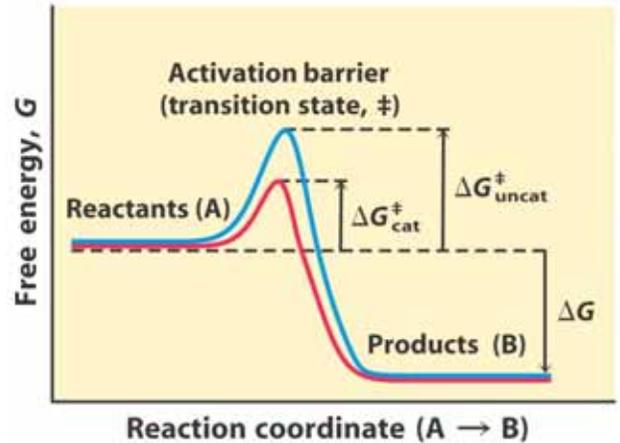
Carolus Linnaeus – classification of
organisms by anatomic similarities

Charles Darwin – the origin of different
species thru evolution

Biochemistry – the molecular anatomy of
cells

Eg sequence of the *genome* (composed of all
the *genes*)

Terms comparing genes:

Homologous genes = genes similar in
sequence ; the proteins they encode
=homologs

2 homologous genes in <u>same</u> species:
the species are "paralogous"
their protein products are *paralogs*

(probably due to gene duplication and these
2 genes diverge gradually from mutations)

2 homologous genes or proteins found in
different species : orthologous, orthologs

the variation between homologous genes is a
measure of the divergence of the species